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Ozone Damage to Crops in Southern Africa: An Initial Modeling Study

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Abstract

The Cross Border Impact Assessment Project (CAPIA) was designed to develop an understanding of regional surface ozone concentrations and their potential risk to agriculture in southern Africa. Surface ozone concentrations were estimated using the Comprehensive Air Quality Model with extensions (CAMx). The initial assessment of ozone risk to maize was characterised using the Accumulated exposure Over a Threshold of 40 ppb (AOT40). Modelled ozone concentrations exceed 40 ppb over much of suothern Africa, suggesting that the potential for ozone damage to maize exists across the region. The AOT40 approach has limitations; the most notable being its inability to account for modifying factors that limit the amount of pollutnat taken up by the plant. The aim of this research is to investigate the feasibility of including the stomatal flux algorithms in the CAMx model, and so improve the estimates of ozone uptake in plants and the subsequent risk of ozone damage posed to crops. The initial model results indicate that the areas with elevated ozone concentrations are not the same as those with the highest ozone fluxes, suggesting that application of the more biologically relevant flux-based risk assessment methods would identify different regions within the modelling domain where damage to maize is more likely to occur. In addition, the algorithms in CAMx tend to underestimate both the deposition velocity and ozone flux in comparison to the flux method. Lastly, the maximum modelled total ozone fluxes are above the critical stomatal flux values of 6 nmol m^{-2} s^{-1} currently defined and applied within Europe to assess risk and economic impacts of ozone to agricultural crops.

Introduction

In many parts of the world surface ozone is considered to be the most prevalent and damaging air pollutant to which plants are exposed (Emberson *et al*, 2001a). Precursor emissions from multiple source types in the southern African region include those from biomass burning (Scholes *et al*, 1996), large and small industry and mining, transport ((Fleming and van der Merwe, 2002) and the combustion of wood and fossil fuels in domestic areas. In addition, natural emissions from biogenic sources have been shown to be significant (Greenberg *et al*, 2003; Harley *et al*, 2003). With high insolation and a dominant anticyclonic circulation that imposes long atmospheric residence times for the mixture of pollutants, an ideal environment exists in which ozone can form. Indeed, monitoring at Maun, a remote rural site in Botswana (Zunckel *et al*, 2004) has indicated that ozone concentrations in this remote area often exceed those typically experienced in urban environments. Despite this, surface ozone is monitored at only a few sites. With the exception of the Global Atmosphere Watch station at Cape Point where surface ozone concentrations have been logged since 1983 (Brunke and Scheel, 1998), the measurement records cover relatively short time periods. This dearth of ozone data implies that the understanding of surface ozone concentrations over the region is limited as is the understanding of potential impacts on vegetation.

Following suggestions by van Tienhoven *et al* (2005) that southern African vegetation may be at risk to damage by ozone, the Cross Border Air Pollution Impact Assessment (CAPIA) project was designed to develop an understanding of regional scale surface ozone concentrations, and to assess the potential risk of air pollution on agriculture. In the absence of comprehensive monitored ozone data, a modelling approach was required to meet the objectives of CAPIA. Using available data on anthropogenic and biogenic emissions and regional scale meteorology, ambient surface ozone concentrations were estimated using the Comprehensive Air Quality Model with Extensions (CAMx) (ENVIRON, 2003). The European approach known as the Accumulated exposure Over a Threshold of 40 ppb (AOT40) (Fuhrer *et a*l. 1997) was used to assess the risk to maize in the CAPIA project. van Tienhoven *et al* (2006 identified that the AOT40 was exceeded over large areas of southern Africa and suggested that maize and other agricultural crops were indeed at risk to ozone damage.

The AOT40 is an approach that identifies the potential risk of ozone damage to vegetation based on the ambient concentration to which the plant is exposed (Fuhrer et al. 1997). This approach has some limitations; the most notable being its inability to account for modifying factors that limit the amount of pollutant actually taken up by the plant. These generally occur through modifications to stomatal conductance caused by local environmental conditions such as low humdities and high soil water stresses (Musselman and Massman, 1999). These factors are not considered by the AOT40 approach since damage is only related to the external pollutant concentration rather than the absorbed pollutant dose. The limitations of using only the AOT40 approach for the CAPIA risk assessments were recognised and resulted in the decision to use the recently developed "flux based" risk assessment method

This paper provides an overview of the theory and standard approach used in CAMx to calculate dry deposition of ozone. It also provides a theoretical discussion of the "flux modelling", emphasising the differences between the two methodologies. An initial comparison between ambient concentrations calculated using the standard CAMx dry deposition for ozone and the flux algorithms are presented.

Methods

Dry Deposition Modelling in CAMx

Analogous to an electrical circuit, the movement of aerosols or gases through a plant canopy and onto plant surfaces and the ground surface is typically modelled as a combination of resistances in series and parallel. Each branch of the circuit represents a different path by which material may be deposited. For example, pollutants may transfer to the sites of biological action within the leaves of the plant canopy through the stomatal openings to the mesophyll tissue. They may also deposit on the external surfaces of the plant canopy or move through the canopy and deposit directly on the ground surface. As ozone is a gas, this discussion considers deposition of gases only.

The factor that links the rate of dry deposition of a gas to the ambient concentration is the deposition velocity, where

$$F = -V_d * C \qquad \text{(Eq. 1)}$$

C is the ambient concentration of the gas, V_d is the deposition velocity and F is the deposition rate or flux. The negative notation indicates a downward flux. The ambient concentration is typically measured or modelled, the latter being the case within the CAPIA project. Wesley and Hicks (1977) and later Wesley (1989) developed a resistance model that incorporates the major resistances to deposition which may be described by the following equation:

$$V_d = \frac{1}{R_a + R_b + R_s} \qquad \text{(Eq. 2)}$$

R_a is the aerodynamic resistance and represents bulk transport between some reference height and the plant canopy. In the case of the CAMx modelling performed within the CAPIA project this height is 10 m above the ground surface. The pollutant transport within this part of the atmosphere results from turbulent diffusion. The magnitude of the R_a term depends on the intensity of turbulent motion, which in turn, depends on insolation, wind speed, surface roughness and the near-surface lapse temperature rate. As a result, R_a is a minimum on warm sunny days with strong mixing induced by surface heating and mechanical turbulence and a maximum on cool nights with calm winds and suppressed mixing.

In CAMx (ENVIRON, 2003) R_a is calculated from:

$$R_a = \frac{1}{ku_*}\left[\ln\left(\frac{z}{z_0}\right) - \Phi_h\right] \qquad \text{(Eq. 3)}$$

where

u_*	frictional velocity (m/s), which is a function of the landuse type which is an input requirement in CAMx.
k	von Karman constant.
z	reference height (10m)

z_0 roughness length, which is also a function of landuse.
Φ_h stability correction term.

R_b is the quasi-laminar sub-layer resistance that represents molecular diffusion through the thin layer of air that is directly in contact with the surface to which deposition takes place. It is mostly dependant on the molecular diffusivity of each pollutant species, which in turn is dependant on the friction velocity (u_*), von Karman's constant (k) and the Schmidt number (S_c) which is the ratio of air viscosity to molecular diffusivity of the chemical species.

$$R_b = \frac{2S_c^{2/3}}{ku_*} \qquad \text{(Eq. 4)}$$

The surface resistance, R_s, is expressed as a combination of serial and parallel resistances that depend on the physical and chemical characteristics of the surface in question. Over vegetated land surfaces R_s is given by the following equation:

$$R_s = \frac{1}{\frac{1}{r_{st}+r_m} + \frac{1}{r_{uc}} + \frac{1}{r_{dc}+r_{cl}} + \frac{1}{r_{ac}+r_{gs}}} \qquad \text{(Eq. 5)}$$

The first serial resistance represents the pathway into the stomatal and mesophyllic portions of the active plant. The second resistance represents the pathway into the upper canopy and the third is the pathway into the lower canopy. The fourth resistance is the pathway to the ground surface. Some of the resistances are dependant on season and landuse type which are included in the dry deposition model (Wesley, 1989), and so included in CAMx. Other resistances are adjusted in CAMx to account for variation in insolation, moisture stress and surface wetness.

The CAMx modelling domain is typically divided into user defined spatial grids. The underlying surface is gridded accordingly and variations in land use type across the modelling domain are captured in the model by the allocation of the dominant land use category to each grid block. The plant specific resistance algorithms described above are then scaled-up by applying them in each grid block.

The European Flux Model

In the European flux model, total ozone deposition velocity is also calculated using the 3-resistance formulation (Eq.2), similar to Wesley's (1986) method which is used in CAMx. The resistances include the aerodynamic resistance (R_a), the boundary layer resistance (R_b) and the surface resistance (R_{sur}). R_a and R_b are calculated using the same principles described in equations 3 and 4 respectively. R_{sur} comprises a plant canopy resistance and a resistance to the underlying soil similar to the Wesley (1989) approach. It is given by:

$$R_{sur} = \frac{1}{\frac{LAI}{R_{sto}} + \frac{LAI}{R_{ext}} + \frac{1}{R_{inc}+R_{soil}}} \qquad \text{(Eq. 6)}$$

where

R_{inc} canopy aerodynamic resistance
R_{soil} soil resistance
R_{ext} external resistance
R_{sto} land cover-specific stomatal resistance which is the resistance to ozone uptake through the stomata
LAI leaf area index,

R_{ext} and R_{soil} are constants. R_{inc} is calculated with:

$$R_{inc} = \frac{(b * LAI * h)}{u_*} \qquad \text{(Eq. 7)}$$

where

b an empirical constant taken as 14 m^{-1}
h the vegetation height
u_* friction velocity

A schematic of the various resistances and their configuration is presented in Figure 1.

One of the key differences between the CAMx and European deposition models is the approach to calculating stomatal resistance. To incorporate certain aspects of the European deposition model into the CAMx model two modules were developed. Module 1 is a canopy stomatal resistance module and Module 2 is a leaf stomatal flux module. The application of the former can be used to calculate total dry deposition to maize using the stomatal formulations that are unique to the European deposition model. This will allow comparisons of dry deposition to maize that are solely dependant upon the calculation of the stomatal component, considered a key component of total deposition during the growing season. The application of Module 2 would give an indication of the ozone uptake to upper canopy leaves of maize. Comparisons of the spatial pattern of cumulative ozone flux with AOT40 could then be used to assess the consequences of using concentration rather than flux based approaches to identify the risk posed to vegetation from surface ozone.

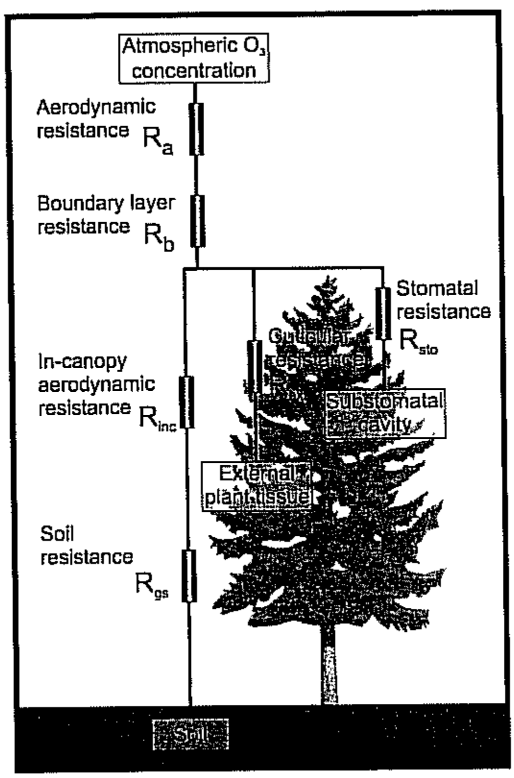

Figure 1: A schematic of the resistances to dry deposition of a pollutant gas (Emberson *et al.* 2001b)

Module 1 was developed to take the place of the existing stomatal resistance (defined by r_{st} in CAMx as in Eq. 8). The existing r_{st} is used to estimate surface resistance and is incorporated in the overall resistance scheme according to the parallel resistance approach of Wesley and Hicks (1977) and Wesley (1989). The stomatal resistance (r_{st}) is calculated with:

$$r_{st} = \text{diffract} * r_j * (1 + (200 / (\text{solflux} + 0.1))^2) * (400 / (t_s * (40 - t_s))) \quad \text{(Eq. 8)}$$

where

diffract	ratio of molecular diffusivity of water to species;
r_j	baseline minimum stomatal resistance (s/m);
solflux	solar radiation flux (W m^{-2});
t_s	surface temperature (°C).

In the European flux model Module 1 replaces the calculation of r_{st} (described above) with R_{sto} (described below). Module 2 calculates g_{sto} (stomatal conductance in mmol O_3 m^{-2} s^{-1} on a projected leaf area basis). From the latter, stomatal ozone flux to a representative leaf at the top of the canopy could be calculated.

Parameters that are applied in the Module 1 and 2 for maize are listed in Table 1.

Module 1: Canopy Stomatal resistance (R_{sto})

Module 1 calculates canopy stomatal resistance (R_{sto}) in units of s m^{-1} according to :-

$$R_{sto} = [(g_{max} * f_{phen} * f_{light} * \max\{f_{min}, (f_{temp} * f_{VPD} * f_{SWP})\}) / 41000]^{-1} \qquad \text{(Eq. 9)}$$

41000 is the factor to convert from mmol m^{-2} s^{-1} to m s^{-1} (Jones, 1992).

g_{max}	is the maximum stomatal conductance in units of mmol O_3 m^{-2} s^{-1} expressed on a projected leaf area basis
f_{phen}	is the relative f determined by leaf age
f_{min}	is the minimum daytime stomatal conductance observed under field conditions
f_{light}	is the relative mean canopy f determined by irradiance
f_{temp}	is the relative f determined by temperature
f_{VPD}	is the relative f determined by the leaf-to-air vapour pressure deficit (VPD)
f_{SWP}	is the relative f determined by the soil water potential (SWP), (related to soil moisture deficit, SMD)

The relative g factors are expressed on a scale of 0-1 and used to modify g_{max}. Capitals denote the whole canopy value; small case denotes a single leaf.

The variables required to calculate R_{sto} in Eq. 10 are either assigned constant values (Table 1) or calculated using the following set of equations:

Table 1: Parameters applied in the calculation of R_{sto} and g_{sto}.

Parameter	Description	Value	Unit
R_{ext}	Resistance of the exterior plant parts to uptake or destruction of ozone	2500	s/m
R_{soil}	Resistance to destruction or absorption at the soil surface	200	s/m
LAI_{max}	Maximum LAI during the growing season	3.5	M^2/m^2
h	Maximum plant height	2	M
g_{max}	maximum stomatal conductance in units of mmol O_3 m^{-2} s^{-1} expressed on a projected leaf area basis	150	mmol O_3 m^{-2} s^{-1} (P)
f_{phen}	Relative g determined by leaf age	1	
f_{min}	Minimum daytime stomatal conductance observed under field conditions	0.2	
f_{light}	relative mean canopy g determined by irradiance	see function	
α	for f_{light} function	-0.005	
f_{temp}	relative g determined by temperature	see function	
T_{min}	for f_{temp} function	0	
T_{opt}	for f_{temp} function	25	
T_{max}	for f_{temp} function	51	
f_{VPD}	relative g determined by the leaf-to-air vapour pressure deficit (VPD)	see function	
VPD_{max}	for f_{VPD} function	1	
VPD_{min}	for f_{VPD} function	2.5	
f_{SWP}	relative g determined by the soil water potential (SWP), (related to soil moisture deficit, SMD)	see functions	

Irradiance (f_{light})

For Module 1, the application of a canopy radiative transfer model is necessary to estimate the influence of irradiance (which changes with canopy depth) on the stomatal conductance (g_{sto}) of sunlit and shaded leaf portions of the canopy.

The f_{light} function requires radiation measured as phothsynthetically active radiation (PAR) in μmol m^{-2} s^{-1}.

$$\text{PAR } (\mu\text{mol m}^{-2}\text{ s}^{-1}) = \text{Solar radiation } (\text{Wm}^{-2}) / 2 * 4.57 \qquad \text{(Eq. 10)}$$

Application of the canopy radiative transfer model requires the evaluation of the solar elevation (sinβ) to relate the "height" of the sun in the sky with the penetration of irradiance into the canopy. sinß is calculated according to the following equation, with angles in degrees.

$$\text{solar declination } (\delta) = -23.4 * \text{COS}(360*(\text{day of year}+10)/365) \qquad \text{(Eq. 11)}$$

$$\sin\beta = \sin(\text{latitude})*\sin(\delta)+\cos(\text{latitude})*\cos(\delta)+\text{time of day function} \qquad \text{(Eq. 12)}$$

The canopy radiative transfer model is used to estimate the PAR for both sunlit and shaded canopy portions. This requires that the Idir and Idiff fractions of the total PAR are calculated. This is achieved using a simplified version of the method developed by Weiss & Norman (1985) to estimate the fraction of PAR that is direct irradiance (If_{dir}) using equation 14. The remaining fraction being the diffuse irradiance component (If_{diff}):-

$$If_{dir} = -0.000000084 * PAR^2 + 0.00041 * PAR + 0.4075 \qquad \text{(Eq. 13)}$$

$$If_{diff} = 1 - If_{dir} \qquad \text{(Eq. 14)}$$

The respective fractions of direct and diffuse irradiance can then be used to estimate the absolute irradiance at the top of the canopy.

$$I_{dir} = If_{dir} * PAR \qquad \text{(Eq. 15)}$$

$$I_{diff} = If_{diff} * PAR \qquad \text{(Eq. 16)}$$

The necessary input parameters are then available to apply the canopy radiative transfer model so that the irradiance falling on the sunlit and shaded portions of the canopy as a whole can be estimated:-

$$PAR_{shade} = I_{diff} * \exp(-0.5 * LAI^{0.7}) + 0.07 * I_{dir} * (1.1 - 0.1 * LAI) * \exp[-\sin\beta] \qquad \text{(Eq. 17)}$$

I_{diff} is the flux density of diffuse PAR above the canopy. LAI is the leaf area index

$$PAR_{sun} = I_{dir} * \cos(\theta) / \sin\beta + PAR_{shade} \qquad \text{(Eq. 18)}$$

I_{dir} is the flux density of direct PAR above the canopy.

θ is the angle between a leaf and the sun and is assumed to be constant to 60 degrees.

PAR_{sun} and PAR_{shade} are the flux densities of PAR on sun and shaded leaves. Scaling from the leaf to canopy level is achieved by calculating f_{light} [equation 20 to 24] for sunlit and shaded fractions proportionally (in terms of LAI) for the whole canopy. Where:

$$f_{light}sun = [1 - \exp(\alpha * PAR_{sun})] \qquad \text{(Eq. 19)}$$

$$f_{light}shade = [1 - \exp(\alpha * PAR_{shade})] \qquad \text{(Eq. 20)}$$

$$LAI_{sun} = [1 - \exp(-0.5 * LAI / \sin\beta)] * 2 \sin\beta \qquad \text{(Eq. 21)}$$

$$LAI_{shade} = LAI - LAI_{sun} \qquad \text{(Eq. 22)}$$

$$f_{light} = f_{light}sun * LAI_{sun} / LAI + f_{light}shade * LAI_{shade} / LAI \qquad \text{(Eq. 23)}$$

$f_{light}sun$ is the f_{light} value for sunlit leaves
LAI_{sun} is the sunlit leaf area of the canopy.
LAI_{shade} is the shaded area of the canopy
LAI is the leaf area index
$f_{light}shade$ is the f_{light} value for shaded leaves

Temperature function (f_{temp})

The f_{temp} function estimates the influence of temperature on g_{sto}. Here it is assumed that temperature is constant with depth throughout the canopy.

$$f_{temp} = \max\{f_{min}, [(T-T_{min}) / (T_{opt}-T_{min})] * [(T_{max}-T) / (T_{max}-T_{opt})]^{bt}\} \qquad \text{(Eq. 24)}$$

T is the air temperature in °C,

T_{min} and T_{max} are the minimum and maximum temperatures at which stomatal closure occurs to f_{min},

T_{opt} is the optimum temperature and

bt is defined as: $bt = (T_{max}-T_{opt}) / (T_{opt}-T_{min})$

Vapour Pressure Deficit function (f_{VPD})

The f_{VPD} function estimates the influence of Vapour Pressure Deficit (VPD) on g_{sto}. Input data available from CAMx are water vapour mixing ration in ppm (w_p) and atmospheric pressure in hPa (p).

Vapour pressure is calculated using the following equations:-

Calculate water vapour in g/kg (w_s)

$$w_s = (w_p * 1000) / 10^6 \quad \text{(Eq. 25)}$$

Calculate vapour pressure in hPa (e)

$$e = \frac{w_s * p}{1000 * 0.622} \quad \text{(Eq. 26)}$$

Saturated vapour pressure (e_s) in hPa which is a function of temperature is required to convert from vapour pressure to vapour pressure deficit.

$$e_s = 611.21 * \exp\left(\frac{17.502 * T}{240.97 + T}\right) / 100 \quad \text{(Eq. 27)}$$

e_s, the saturation vapour pressure is in Pa. T is the air temperature in °C.

The calculation of vapour pressure deficit, VPD, in kPa is then

$$VPD = \min\{0, (e_s - e)/100\} \quad \text{(Eq. 28)}$$

The resulting VPD value (divided by 1000 to give VPD in kPa) can then be used in the following f_{VPD} function:-

$$f_{VPD} = \min\{1, \max\{f_{min}, ((1-f_{min}) * (VPD_{min} - VPD) / (VPD_{min} - VPD_{max})) + f_{min}\}\} \quad \text{(Eq. 29)}$$

Soil water status (f_{SWP})

The CAMx model identifies three levels of soil water potential; these are assigned to the following f_{SWP} values, where f_{SWP} represents the function deterring the influence of soil water status on g_{sto}. Although this is a simplification of the model, only allowing step-changes in g_{sto} response to SWP it will provide a spatial indication of the relative importance of the SWP component.

No water stress / irrigated crops $f_{SWP} = 1$

Medium water stress $f_{SWP} = 0.5$ (Eq. 30)

Extreme water stress $f_{SWP} = f_{min}$

Module 2: Leaf stomatal conductance (g_{sto})

Module 2 calculates g_{sto} (stomatal conductance in mmol O_3 m^{-2} s^{-1} on a projected leaf area basis). From this stomatal ozone flux to a representative leaf at the top of the canopy can be evaluated.

$$g_{sto} = (g_{max} * f_{phen} * f_{light} * \max\{f_{min}, (f_{temp} * f_{VPD} * f_{SWP})\} \quad \text{(Eq. 31)}$$

With the exception of g_{sto}, the only other variation between Module 1 and Module 2 is in the calculation of irradiance, f_{light}. For Module 1 the application of a canopy radiative transfer model is necessary to estimate the influence of irradiance (which changes with canopy depth) on the stomatal conductance of sunlit and shaded leaf portions of the canopy. For module 2, stomatal conductance is estimated only for a leaf in the upper canopy and hence can be calculated simply as a function of the irradiance reaching the top of the canopy as follows:

$$f_{light} = 1 - \exp(\alpha * PAR) \quad \text{(Eq. 32)}$$

PAR is the phothsynthetically active radiation and α is constant for f_{light}.

The calculation of top leaf stomatal ozone flux ($fluxO_3$) can then be made using Eq. 33.

$$fluxO_3 = g_{sto} * O_3 \quad \text{(Eq. 33)}$$

Results and Discussion

As an initial method of comparing the CAMx and flux methodologies, a single 50 x 50 km model grid cell over Zimbabwe was selected to investigate model outputs from a 5-day period covering the 10 to 14 January 2001. The results in Fig 3 (top) show clearly the diurnal variation in ozone concentration over Mashonaland, with concentrations reaching more than 90 ppb in the middle of the day. As may be expected, the deposition velocities (Vd) calculated with both the CAMx and the European methodologies (Fig 3, middle) also show strong diurnal variations.However, the V_d values estimated using the European method are consistently higher than those calculated using the CAMx routine during the daytime periods.

Due to the relationship between the ambient concentration and V_d, the resultant ozone flux is low at night and reaches maximum values during the daytime period. The European flux model values are consistently greater than those estimated using CAMx. For CAMx, ozone fluxes range from 0 to about 6 nmol O_3 m^{-2} s^{-1}, compared with the European method values, which range from near zero values at night to average daytime maxima of more than 10 nmol O_3 m^{-2} s^{-1} , reaching more than 15 nmol O_3 m^{-2} s^{-1} on 13 January 2001. The higher ozone fluxes estimated using the European model most likely reflect the higher maximum stomatal conductance value assigned to maize in the European model.

It is also interesting to note that the two days with the highest ozone concentrations (10 (0 to 24 hours) and 11 January (24 -48 hours)) are not always those with the highest calculated ozone fluxes. This apparent incongruity would possibly be even more striking if stomatal fluxes were compared with ozone concentrations and highlights the need to use flux rather than concentration based approaches for ozone risk assessments.

The comparison is expanded to a portion of the maize producing area of Mashonaland West to Mashonaland East and Mashonaland Central in Zimbabwe. Here a 550 km by 550 km 'window' is extracted from the southern Africa modelling domain. In Fig 4 each panel represents an area of approximately 300 000 km^2, running from grid cell 33 to 44 in an east to west direction and from 34 to 44 in a south to north direction. A single modelled value represents each cell. Unlike the diurnal depiction in Fig. 3, the results shown in Fig. 4 are a snap-shot over the defined domain showing results for a single hour, namely 16:00 on 10 January 2001.

For this hour the modelled concentrations of ozone range between 20 and 100 ppb over the model window (Fig. 3, left). Concentrations exceed the threshold value of 40 ppb suggesting that damage to vegetation may be expected over an extensive area covering almost the entire southern half of the window.

One might expect high ozone fluxes to coincide with areas of high ozone concentrations, given the relationship in Eq. 1. Generally speaking this assumption is valid for the CAMx deposition (Fig. 3, centre) with the highest fluxes occurring over the southern parts of the window, ranging from low values and reaching 6 nmol O_3 m^{-2} s^{-1}. It is not a perfect match however, and the area of maximum fluxes occur to the south of the maximum ambient concentrations. The amount of damage predicted by ozone flux models depends on the toxicity of the absorbed dose. The toxicity levels of absorbed ozone to maize growing in southern Africa is not yet known, but European work for wheat and potato has shown that damage could occur at fluxes above 6 nmol m^{-2} s^{-1}.

As seen in Fig. 3 for the modelling period in cell 38:38, the ozone flux estimated with the European method is consistently higher than that estimated with the CAMx methodology (Fig. 4 centre and right) though there is agreement in the general area where the ozone flux is highest. However, the European model also identifies areas of high ozone fluxes in the northeastern parts of the window (Fig. 4, right).

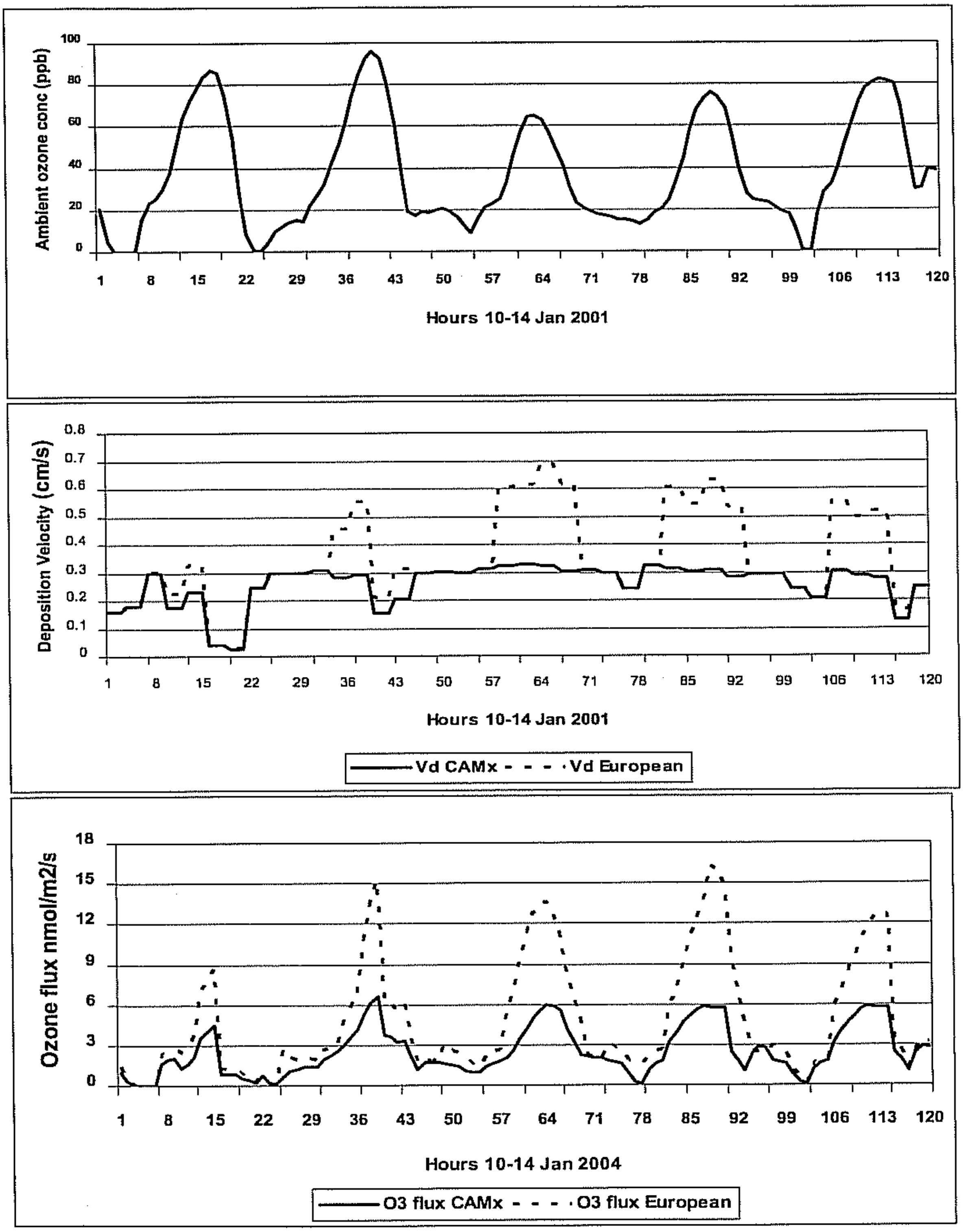

Figure 3: Model results for cell (38:38) in Zimbabwe for 120 hour modelling period 10 to 14 January 2001 with ozone concentration in ppb (top), and the corresponding deposition velocities (centre), and total ozone fluxes (bottom) the latter two components calculated with both the CAMx and European methodologies.

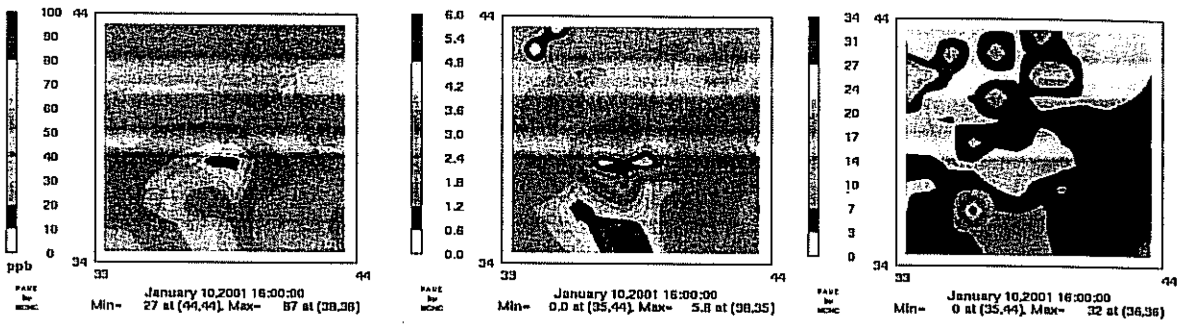

Figure 4: Modelled ambient ozone concentrations in ppb (left). Modelled CAMx total ozone flux (centre) and modelled flux using the European stomatal flux algorithms over Mashonaland, Zimbabwe at 16:00 on 10 January 2001. Values given in nmol O_3 m^{-2} s^{-1}.

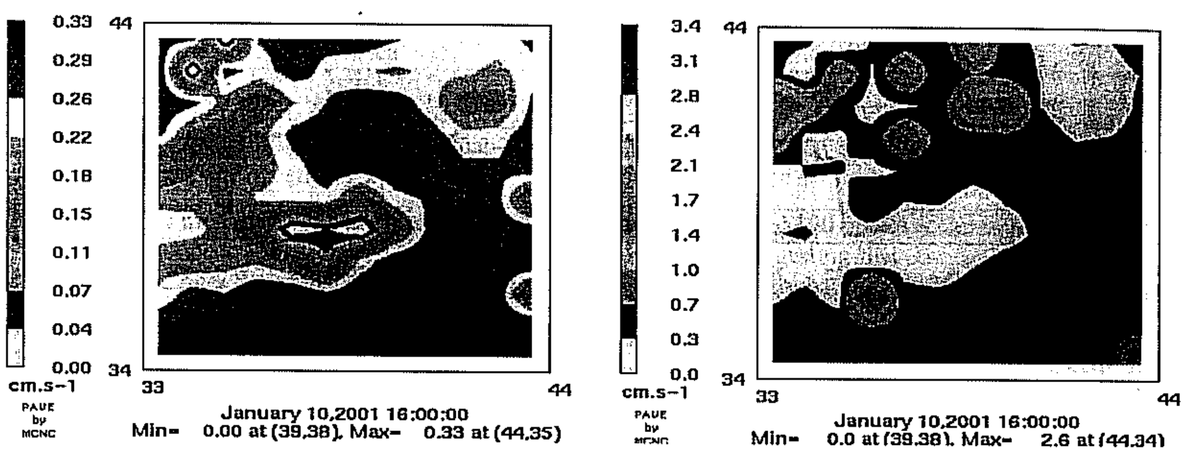

Figure 5: Modelled ozone deposition velocity in cm s^{-1} over Mashonaland, Zimbabwe at 16:00on 10 January 2001, estimated with the CAMx (left) and the European flux algorithm (right).

An interesting comparison is made when evaluating the modelled CAMx ozone fluxes (Fig. 4 centre) and the European ozone fluxes (Fig. 4 right). Again the maximum flux occurs in the south of the window where rates range between 3 and 6 nmol O_3 m^{-2} s^{-1} for the CAMx routine. These are generally higher for the European method with ozone fluxes in the south ranging from 3 to more than 30 nmol O_3 m^{-2} s^{-1} in one particular area. This is most likely due to the European model being parameterised specifically for maize rather than a more generalised "agricultural" land-cover type. Also interesting is the area of relatively higher ozone fluxes in the northwestern parts of the window predicted using the European method that coincides with relatively low ambient ozone concentrations. This suggests that the incorporation of additional environmental parameters using the European method is able to identify instances when lower ozone concentrations are capable of producing higher ozone fluxes due to the low resistance to ozone uptake and deposition. The European flux estimates reach 14 nmol O_3 m^{-2} s^{-1}.

Examination of the deposition velocities (V_d) (Fig. 5) adds some additional insights. Again, V_d calculated with the CAMx algorithms is consistently lower than the European method at 16:00 on 10 January, also seen in Fig. 3. Both approaches return V_d values in the region of 0.3 cm s^{-1} over the largest part of the window, but the maximums returned with the European method are much higher than that with CAMx. The highest CAMx values occur in the southwestern part of the window, in the region of 0.35 cm s^{-1}, decreasing almost consistently towards the northeast. The European flux model shows a contrasting picture with patches of higher V_d ranging between 0.3 and 1.7 cm s^{-1}, with high deposition velocities in the south and in the north east, coinciding with the observed maximums of ozone flux (Fig. 4, right). It is useful to make preliminary comparisons of the model output values with deposition velocities for maize measured under field conditions to give some indication of how well the different models are performing. Deposition velocities for maize growing in The Netherlands were measured by van Pul & Jacobs (1994). These measurement data found V_d values in the range of 0.2 to 1.6 cm s^{-1} which would indicate that the predictions of deposition velocity made using the European stomatal flux algorithms are closer to realistic values for this species. However, additional work will be necessary to fully understand the model outputs in relation to observed measurements under location specific climatic conditions.

Conclusions

It is commonly recognised that using concentration based approaches, such as the AOT40, to assess potential damage to agricultural crops has some limitations. The most notable of these are due to the modifying factors that limit the amount of pollutant actually taken up by the plant and hence uncouple the relationship between concentration and damage. These generally occur through modifications to stomatal conductance caused by local environmental conditions such as low humidities and high soil water stresses. These factors are not considered by the AOT40 approach since damage is only related to the external pollutant concentration rather than the absorbed pollutant dose.

As such, a "flux based" risk assessment method (currently being developed as part of an ozone deposition model for use in Europe) has been applied in this work to assess the possibility of using an additional, more biologically relevant risk assessment method within the CAPIA project. The aim of the work was to initiate the application of certain components of the European deposition module in the standard CAMx model, in particular to investigate the feasibility of including the stomatal flux algorithms, and so improve the estimates of ozone uptake in plants and the risk posed to crops.

The modification of the CAMx model has been successfully completed and initial results, using a single day's model output over Zimbabwe, illustrate the perceived risk across the region using both concentration and flux based approaches. Analyses of these data highlight the spatial differences between ambient concentrations as calculated for CAPIA, and ozone fluxes calculated by both the CAMx and European deposition models. The main conclusions of this research are:

- Modelled ambient ozone concentrations exceed the 40 ppb threshold over much of southern Africa. This would suggest that application of the concentration based (AOT40) risk assessment method would indicate the potential for ozone damage to maize in the region.
- The areas where ozone concentrations are elevated are not the same as those with the highest ozone fluxes. This suggests that application of the more biologically relevant flux-based risk assessment methods would identify different regions within the modelling domain as being those where most damage to maize is likely to occur.
- The CAMx model tends to underestimate both the deposition velocity and actual ozone flux in comparison to the flux method. This is most likely due to the flux method modelling for a specific species (i.e. maize) rather than a more generic land-cover type (i.e. agricultural crops).
- The maximum total ozone fluxes are above the critical stomatal flux values of 6 nmol m^{-2} s^{-1} currently defined and applied within Europe to assess risk and economic impacts of ozone to agricultural crops.

This preliminary work has shown that both the concentration and flux based approaches indicate that ground level ozone concentrations could result in damage to maize across southern Africa. However, the areas of maize growing identified as being at most risk from ozone varies spatially dependant upon which of the two approaches are used. This is due to the flux-based method reducing the uncertainty of the risk assessment by incorporating modifying factors and relating potential damage to absorbed dose rather than concentration. The initial work has also shown there to be differences between the current approaches to estimating deposition in CAMx compared to the species-specific modelling conducted using the European approach. It is important that the initial work is expanded in order to develop improved understandings of ozone deposition and uptake by agricultural crops.

References

Emberson L. D., Ashmore M. R., Murray F., Kuylenstierna J. C. I., Percy K. E., Izuta T., Zheng H., Sheu B. H., Liu C. P., Agrawal M., Wahid A., Abdel-Latif N. M, van Tienhoven M, de Bauer L. I. and Domingos, 2001a. Impacts of air pollutants on vegetation in developing countries, *Water, Air and Soil Pollution*, 130, 107-118.

Emberson L.D., Ashmore M.R., Simpson D., Tuovinen J.-P., and Cambridge H.M., 2001b Modelling and mapping ozone deposition in Europe. *Water, Air and Soil Pollution,* 130, 577-582.

ENVIRON, 2003. User's guide to the Comprehensive Air Quality Model with Extensions (CAMx), ENVIRON International Corporation, 101 Rowland Way, Novato, CA 94945.

Fleming G. and van der Merwe M., 2002. Spatial disaggregation of greenhouse gas emissions inventory data for Africa south of the equator, http://gis.esri.com/library

Fuhrer, J., Skärby, L., and Ashmore, M.R., 1997, Critical levels for ozone effects on vegetation in Europe. *Environmental Pollution*, 97 (1-2), 91-106.

Greenberg J.P, Guenther A., Harley P., Otter L., Veenendaal E. M., Hewitt C. N., James A. E. and Owen S. M., 2003. Eddy flux and leaf-level measurement of biogenic VOC emissions from mopane woodland of Botswana, *Journal of Geophysical Research*, 108(D13), 8 466, doi:10.1029/2002JD002317,2003.

Harley P., Otter L., Guenther A. and Greenberg J., 2003. Micrometeorological and leaf-level measurements of isoprene emissions from a southern African savanna, *Journal of Geophysical Research*, 108(D13), 8 468, doi:10.1029/2002JD002592,2003.

Scholes R. J., Kendall J. and Justice C. O., 1996. Emissions of trace gases and aerosol particles due to vegetation burning in southern Africa, *Journal of Geophysical Research*, 101, D19, 23 677-23 682.

van Pul W.A.J. and Jacobs A.F.G. (1994) The conductance of a maize crop and the underlying soil to ozone under various environmental conditions, Boundary-Layer Meteorology, 69, 83-99.

Wesley M. L. and Hicks B.B., 1977, Some Factors that affect the deposition rates of sulphur dioxide and similar gases on vegetation, Journal of the Air Pollution Control Association, 27(11), 1110-1116.

Wesley M. L., 1989. Paramererization of surface resistance to gaseous dry deposition in regional-scale numerical models, *Atmospheric Environment*, 23, 1293-1304.

van Tienhoven A. M., Otter L., Lenkopane M., Venjonoka, K and Zunckel M., 2005. Assessment of ozone impacts on vegetation in southern Africa and directions for future research, *South African Journal of Science,* 101, 143-148.

van Tienhoven A. M., Zunckel M., Emberson L., Koosailee, A. and Otter L., 2005. Preliminary assessment of ozone impacts to maize (*Zea Mays*) in southern Africa, *Environmental Pollution*, 140(2006), 220-230.

Zunckel M., Venjonoka K., Pienaar J. J., Brunke E-G., Pretorius O., Koosaliee A., Raghunandan A. and. van Tienhoven M. A., 2004. Surface ozone over southern Africa: Synthesis of monitoring results during the Cross Border Impact Assessment project, *Atmospheric Environment*, 38(2004), 6139-6147.